PATENT SPECIFICATION (11) 1 225 406

1225406

NO DRAWINGS

(21) Application No. 36773/68 (22) Filed 1 Aug. 1968
(31) Convention Application No. 657540 (32) Filed 1 Aug. 1967 in
(33) United States of America (US)
(45) Complete Specification published 17 March 1971
(51) International Classification G 03 c 5/00
(52) Index at acceptance
G2C C10A3 C10B C9B

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(54) METHOD OF PROCESSING PHOTOGRAPHIC SILVER HALIDE MATERIALS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of processing photographic materials.

Many photographic processes use image-forming materials comprising a support carrying one or more layers comprising hydrophilic colloids such as gelatin. When such materials are processed by passing through baths of solution in processing machines, as described, for example, in U.S. patent 3,025,779, markings tend to be produced in a definite line pattern at a fixed distance from the leading edge of the material. For example, when film is processed in a roller transport machine having many rollers of the same diameter, each roller tends to produce a line at the same place on the film so that the marking is cumulative.

The markings have been shown to be of two types: one type is due simply to dirt deposition and is referred to as a "simple pi line"; the other type is due to density variations in the developed silver and is referred to as a "chemical pi line". Simple pi lines can be removed by buffing, but no process for removing chemical pi lines has been found so far.

After prolonged use of processing solutions in continuous processing machines, such as roller transport processors, colloidal silver produced as a by-product of development tends to nucleate surface development on photographic materials being processed. This results in an undesirable increase in the fog level of the resulting image.

According to the present invention there is provided a method of processing a photographic silver halide sensitive material which comprises treating the material with an aqueous processing solution containing a sulphonated hemlock tannin polymer.

Also provided in accordance with the invention are photographic materials and processing compositions useful in carrying out the method of the invention.

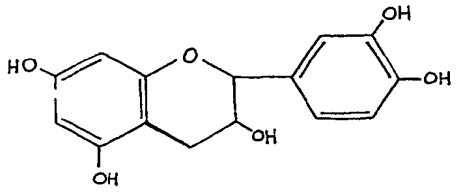
The term "hemlock tannin polymers", as employed herein, refers to a class of polyphenolic compounds typically found in coniferous tree barks, such as the bark of Western hemlock trees (Tsuga heterophylla). The polymers can be extracted with hot water (about 97°C.) from the bark. Hemlock tannin polymers and a suitable method for their preparation are described in, for example, an article by H. L. Hergert, L. E. Van-Blarican, J. C. Steinberg and K. R. Grasy in *Forest Products Journal*, Volume XV, Number 11, November, 1965, pages 485—491. Hemlock tannin polymers can also be prepared by the method described in United States patent 2,782,241 of K. R. Gray and H. L. Crosby, issued February 19, 1957. This method includes extraction of the desired polymeric products with a dilute aqueous alkali metal hydroxide solution at elevated temperature, e.g. 65°C. to 185°C.

The sulphonated hemlock tannin polymers used in the present invention preferably contain at least one sulphonate group, typically an alkali metal sulphonate group (e.g. $—SO_3Na$ or $—SO_3K$) for each repeating unit. The hemlock tannin polymers can be sulphonated using a wide variety of sulphonation processes, such as set out in Noller, *Chemistry of Organic Compounds*, W. B. Saunders and Co.,

[*Price 25p*]

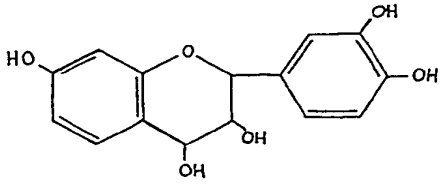
Philadelphia, 1952, including treating the hemlock tannin polymer with sodium sulphite or sulphuric acid.

Preferred sulphonated hemlock tannin polymers are obtained by sulphonating those polymers which are copolymers of catechin:



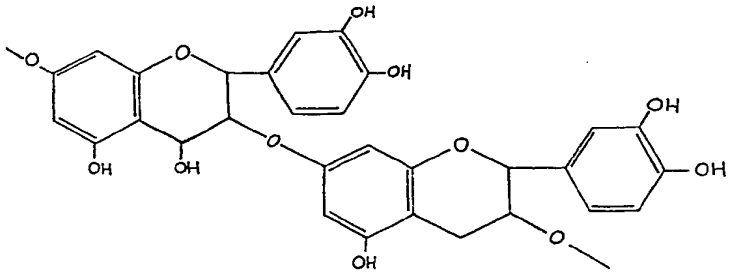
I

with leucocyanidin:



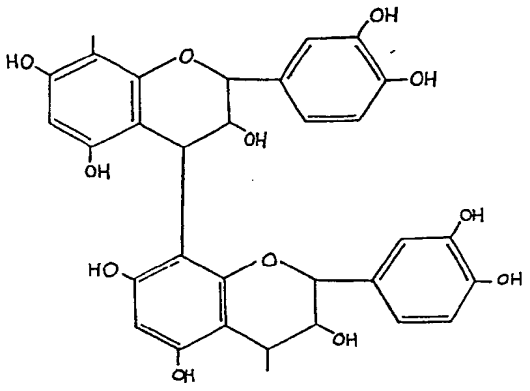
II

having the repeating structural units:



III

and:



IV

The average number of repeating structural units is normally sufficiently high for the polymer to be solid; however, the number is not exactly known. The molecular weight is usually at least 3,000.

A commercially available dispersing agent useful for the method of the invention is sold under the trade name of "Rayflo-C", by Rayonier, Incorporated, New York, United States of America and is a water-soluble mixture of copolymers of catechin with leucocyanidin in sulphonated form. It is a red-brown, free-flowing powder having the following typical chemical characteristics:

Phenolic hydroxyl %	7.8
Methoxy group %	1.4
Sodium %	9.0
Calcium %	0.3
pH (1% by weight aqueous solution)	8.2
Moisture %	4.7

The sulphonated hemlock tannin polymer can be dissolved or incorporated in any suitable manner in an aqueous solution. Thus it can be incorporated in the form of a dry powder, aqueous concentrate, dispersion or aqueous solution, for instance. The processing solution is usually a developing, stabilizing or fixing composition, but other processing solutions such as those for preventing water-spotting, are suitable. Typical processing solutions and their components are disclosed, for example, in Mees, *Theory of the Photographic Process*, Third Edition, MacMillan Company, New York, N.Y., United States of America, (1966).

It is often advantageous to provide separate containers, such as packages or bottles, of the components or mixtures of the components of the processing compositions of the invention for storage before use. These can be in containers in kit form.

The concentration of the dispersing agent required in a particular processing solution should be chosen with regard to the other ingredients, the temperature at which the solution is to be employed and so on. A concentration suitable for a developer, stabilizer, or fixer solution will usually be found to be within the range of from 0.001 to 10 grams per litre. The preferred concentration range is from 0.1 gram to 1.0 gram per litre.

A typical developer solution of the invention is an aqueous solution containing a silver halide developing agent, an activator, e.g., an alkali metal hydroxide, and the sulphonated hemlock tannin polymer.

A typical fixing or stabilizing solution of the invention is an aqueous solution containing a silver halide fixing or silver halide stabilizing agent, and the sulphonated hemlock tannin polymer.

The processing compositions of the invention are particularly suitable for a processing method wherein the photographic material is transported in one continuous motion into and out of at least one processing solution. Suitable apparatus and processing steps are described, for example, in United States patents 3,025,779, 3,078,024, 3,122,086, 3,149,551, 3,156,173, and 3,224,356.

It is preferred to include a coagulant for colloidal silver in a solution used for a continuous process of the invention so as to cause the colloidal silver particles to agglomerate or otherwise form larger particles which can be filtered. Examples of coagulants are compounds represented by the structure R—SH, wherein R is a hydrocarbon radical such as an alkyl (e.g. a lower alkyl i.e. alkyl having up to 4 carbon atoms) radical, or an aryl radical, such as a phenyl, xylyl or benzyl radical. Typical coagulants include cysteine and *o*-mercaptobenzoic acid; coagulant quaternary salts, such as di-isobutylphenoxy ethoxyethyl dimethyl ammonium chloride; and high molecular weight polyethylene resins.

The effectiveness of this action caused by the dispersing agent of the invention, and especially by the combination of the dispersing agent with a coagulant, extends for a significant period of use, e.g. several weeks, and is particularly long-lasting when solutions are filtered to remove particles which adversely effect the processed film.

The amount of coagulant employed can vary depending upon components of the processing solution, temperature, and so on. Normally from 0.01 to 1.0% by weight of the coagulant based on the total weight of the processing solution is suitable.

Any of the usual silver halide developing agents can be used in compositions of the invention including polyhydroxybenzene developing agents (e.g. hydroquinone; alkyl substituted hydroquinones such as t-butylhydroquinone, methylhydroquinone and dimethylhydroquinone; catechol; pyrogallol; chloro substituted hydroquinones such

as chlorohydroquinone and dichlorohydroquinone; and alkoxy substituted hydroquinones (such as methoxy or ethoxy hydroquinone) and aminophenol developing agents (e.g. 2,4-diaminophenols and methylaminophenols); ascorbic acid; pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone, including those described in British Patent 930,572; and acyl derivatives of *p*-aminophenol (such as disclosed in British Patent 1,045,303). Such developing agents can be used alone or jointly.

The concentration of the silver halide developing agent can be varied over a wide range, the concentration required depending upon what other components are present, the desired image and other factors, and can be determined by those skilled in the art. The developing agent can be present in one or more layers of the photographic material to be processed.

Developer compositions of the invention normally contain an activator, such as an alkali metal hydroxide (e.g. sodium, potassium or lithium hydroxide) or an organic amine.

The method of the invention can be carried out over a wide range of temperature. Thus it can be carried out at ambient temperatures, but often it may advantageously be carried out at elevated temperatures, such as temperatures of from 30°C. to 90°C.

The photographic emulsions useful according to the invention include a wide variety of silver halide emulsions including non-spectrally sensitized emulsions, such as X-ray emulsions, and orthochromatic, panchromatic and infrared sensitive emulsions containing spectral sensitizing dyes such as those described in British Specifications 606,141 and 654,690. Spectral sensitizers which can be used include cyanines, merocyanines, styryls and hemicyanines.

The photographic emulsions employed in the practice of the invention can be sensitized using any of the well known techniques in emulsion making, for example, by digesting with naturally active gelatin or various sulphur, selenium, noble metal and/or gold compounds.

The photographic emulsions processed according to the invention, and the compositions employed for processing, can contain the usual photographic addenda, including, for example, hardeners (e.g. alum, or the hardeners described in British Patent 974,317); buffers, including various sulphonamides and boraxes; coating aids, plasticizers; speed increasing compounds, such as quaternary ammonium salts and alkylene oxide polymers (e.g. polyethylene glycols); and stabilizing agents such as sodium sulphite.

The silver halides employed in the practice of the invention include any of the photographic silver halides, such as silver bromide, silver iodide, silver chloride and the mixed silver halides such as silver chlorobromide and silver bromoiodide. Particularly good results are obtained with so-called high contrast photographic emulsions in which the halide comprises at least 50 mole per cent chloride. The emulsions can be those which form latent images predominantly on the surface of the silver halide grains or those which form latent images inside the silver halide crystals, such as described in United States Patent 2,592,250 — Davey and Knott, issued April 8, 1952.

The photographic emulsions processed according to the invention can be coated on a wide variety of supports. Typical supports include films, such as cellulose acetate films, polyethylene terephthalate or other polyester films, polyvinyl acetal films, polystyrene films and polycarbonate films, papers including paper supports which are coated with resinous materials (e.g. coated with polyethylene, polypropylene and/or ethylene-butene copolymers), glass and metal.

The photographic materials processed according to the invention normally contain a layer comprising a hydrophilic water-permeable binder. Suitable binders include gelatin, cellulose derivatives and polymerized vinyl compounds and mixtures of such binding agents. The binding agents can also contain water insoluble polymers, such as polymerized ethylenically unsaturated compounds, e.g. polymers of acrylates and methacrylate.

The compositions of the invention can have a wide range of pH values. The developer compositions are, of course, normally alkaline.

The invention is illustrated by the following Examples:

EXAMPLE 1

Exposed sheets of film containing a silver halide gelatino emulsion of the type normally used in radiography are fed into a roller transport processor, as described in U.S. patent 3,025,779, wherein the transport of the sheets of film through the

processing stages is accomplished by means of rollers which contact both sides of the film.

The developing solution which is employed in the processor consists of:

N-methyl-*p*-aminophenol	2.0	grams
Sodium sulphite, desiccated	90.0	„
Hydroquinone	8.0	„
Sodium carbonate . H_2O	52.5	„
Potassium bromide	5.0	„
Water to make	1.0	litre

In processing, the film transported by the rollers is passed through a tank containing the developer solution, a fixing tank containing ammonium thiosulphate fixer, a water wash tank and then a drier section where the film is hot-air dried.

Sheets of film processed in this manner have horizontal lines of higher than background density a few inches from, and parallel to, the leading edge.

A group of the same films identically exposed are processed employing the above developer solution with the exception that 0.5 gram per litre of solution of sulphonated hemlock tannin polymer is added. The unsulphonated form of this copolymer mixture is represented by the Structures III and IV. After processing in the roller transport processor, all the developed film sheets show no horizontal lines.

EXAMPLE 2

Exposed sheets of film containing a silver halide gelatino emulsion of the type normally used in radiography are processed in a roller transport processor as set out in Example 1. The developer solution employed in the processor consists of:—

1-Phenyl-3-pyrazolidone	3.0	grams
Hydroquinone	20.0	„
Sodium sulphite, desiccated	75.0	„
Sodium metaborate, crystalline	48.0	„
Sodium hydroxide	7.5	„
Potassium bromide	5.0	„
5-Methyl benzotriazole	0.3	„
β-Methylgluteraldehyde bis-sodium bisulphite	15.0	„
Water to make	1.0	litre

It is found that pi markings appear on the leading edges of the sheets processed through the processor employing this developer composition.

When 0.25 gram per litre of a sulphonated hemlock tannin polymer is thoroughly mixed in this developer solution and two sheets of film are then passed through the processor, the processed sheets are free from pi line markings.

In comparison experiments, it was shown that the surface active agents mononaphthalene sulphonic acid, sodium salt (at either 2 or 20 grams per litre), and sulphonated and partially desulphonated lignosulphates (at 2 grams per litre) do not eliminate pi line formation. It was also shown that alkanolamide dispersing agents cause fog.

EXAMPLE 3

The process described in Example 2 is repeated employing 0.001 gram per litre of the dispersing agent in the developing solution. Exposed film processed with this concentration in the developer solution is free of pi line markings.

EXAMPLE 4

The process set out in Example 2 is repeated employing 10.0 grams per litre of the dispersing agent in the developer solution. Exposed film processed with this concentration of dispersing agent in the developer solution is free of pi line markings.

EXAMPLE 5

The procedure set out in Example 2 is repeated. However, besides adding 0.25 gram of the dispersing agent per litre of developing solution, 0.25 gram of the dispersing agent per litre of solution is added to the ammonium thiosulphate fixing solution. The resulting processed film is free of any pi line markings. Similarly good results are obtained with dispersing agent concentrations in the fixing solution between 0.001 and 10 grams per litre.

EXAMPLE 6

The procedure set out in Example 1 is repeated using the same developer solution to which 0.1% by volume of the dispersing agent and 0.1% by volume of cysteine are added. This causes the suspended matter in the developer solution to form particles which are filterable from the developer solution. The minimum density of the photographic emulsion processed through this solution is significantly reduced.

EXAMPLE 7

The procedure described in Example 6 is repeated with the exception that the cysteine is replaced with *o*-mercaptobenzoic acid. Similar results are obtained.

WHAT WE CLAIM IS:—

1. A method of processing a photographic silver halide sensitive material which comprises treating the material with an aqueous processing solution containing a sulphonated hemlock tannin polymer.

2. A method according to Claim 1 wherein the sulphonated polymer is a sulphonation product of a mixture of copolymers of catechin with leucocyanidin.

3. A method according to Claim 2 wherein the copolymers comprise repeating structural units of the Formulae III and IV herein and are sulphonated to an extent providing at least one sulphonate group per structural unit.

4. A method according to Claim 2 wherein the sulphonated polymer as a powder contains approximately 7.8% phenolic hydroxyl groups, 1.4% methoxy groups, 9.0% sodium, 0.3% calcium and 4.7% moisture, by weight, and gives a 1% by weight aqueous solution having a pH of approximately 8.2.

5. A method according to any of the preceding claims wherein the aqueous processing solution contains from 0.001 to 10.0 grams per litre of the sulphonated polymer.

6. A method according to any of the preceding claims wherein the aqueous processing solution is a developed solution containing a silver halide developing agent and an activator therefor.

7. A method according to any of Claims 1 to 5 wherein the aqueous processing solution is a photographic fixing or stabilizing solution.

8. A method according to any of the preceding claims wherein the aqueous processing solution contains a coagulant for colloidal silver.

9. A method according to Claim 8 wherein the coagulant is a compound of formula RSH wherein R is a hydrocarbon radical, a coagulant quaternary salt of a high molecular weight polyethylene resin.

10. A method according to Claim 8 wherein the coagulant is cysteine, *o*-mercaptobenzoic acid or diisobutylphenoxy ethoxyethyl dimethyl ammonium chloride.

11. A method according to any of claims 8 to 10 wherein the aqueous processing solution contains from 0.01 to 1.0% by weight of the coagulant, based on the total weight of the solution.

12. A method according to any of the preceding claims wherein the sensitive material is passed through a continuous transport processing machine.

13. A method according to Claim 12 wherein the machine is a roller transport machine.

14. A method according to any of the preceding claims wherein the aqueous processing solution is at an elevated temperature.

15. A method according to Claim 1 as described in any of the Examples 1 to 7 herein.

16. A sensitive photographic material processed by a method according to any of the preceding claims.

17. A composition for the preparation of an aqueous photographic processing solution, which comprises a photographic processing agent and a sulphonated hemlock tannin polymer.

18. A composition according to Claim 17 for the preparation of a developer solution, wherein the processing agent is a silver halide developing agent, the composition also containing an activator for the developing agent.

19. A composition according to Claim 18 which contains a coagulant for colloidal silver.

20. A composition according to Claim 19 wherein the coagulant is one of the coagulants specified in Claims 9 and 10.

21. A composition according to Claim 17 for the preparation of a fixing or stabilizing solution, wherein the processing agent is a silver halide fixing or stabilizing compound.

22. A composition according to Claim 17 of which the formula is one of those specified in the Examples 1 to 7 herein.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

BNSDOCID: <GB___1225406A__I_>